

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>C30B 33/12, H01L 21/3065</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/04213</b> <b>(43) International Publication Date:</b> 27 January 2000 (27.01.00)
<b>(21) International Application Number:</b> PCT/US99/14922 <b>(22) International Filing Date:</b> 30 June 1999 (30.06.99)  <b>(30) Priority Data:</b> 09/116,621                      16 July 1998 (16.07.98)                      US  <b>(71) Applicant:</b> APPLIED MATERIALS, INC. [US/US]; 3050 Bowers Avenue, Santa Clara, CA 95054 (US).  <b>(72) Inventors:</b> NALLAN, Padmapani; 1235 Wildwood Avenue #322, Sunnyvale, CA 94089 (US). CHINN, Jeffrey; 605 St. Croix Lane, Foster City, CA 94404 (US). YUEN, Stephen; 2435 Ruth Cabral Way, Santa Clara, CA 95050 (US).  <b>(74) Agents:</b> BERNADICOU, Michael, A. et al.; Blakely, Sokoloff, Taylor & Zafman LLP, 7th floor, 12400 Wilshire Boulevard, Los Angeles, CA 90025 (US).		<b>(81) Designated States:</b> JP, KR, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> DOPING-INDEPENDENT SELF-CLEANING ETCH PROCESS FOR POLYSILICON		
<b>(57) Abstract</b>		
<p>A method of etching a layer (28) preferably polysilicon on a substrate (14) comprises the steps of placing the substrate on a support (75) in a process chamber (50). The substrate (45) is exposed to an energized process gas comprising a bromine-containing gas preferably HBr, Br<sub>2</sub> or CH<sub>3</sub>Br, a chlorine-containing gas preferably Cl<sub>2</sub> or HCl, an inorganic fluorinated gas preferably NF<sub>3</sub>, CF<sub>4</sub> or SF<sub>6</sub>, and an oxygen gas optionally diluted with He. The volumetric flow ratio of the gas constituents is selected so that the energized process gas etches regions (28a, b) having different concentrations of dopant in the polysilicon layer (28) at substantially the same etching rate. Optionally, the gas composition is also tailored to simultaneously clean off etch residue from the internal surfaces of a process chamber (50) during etching of the substrate (45).</p> <div style="text-align: right;"> </div> <div style="text-align: right;"> </div>		

*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NI	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

WO 00/04213

PCT/US99/14922

## **DOPING-INDEPENDENT SELF-CLEANING ETCH PROCESS FOR POLYSILICON**

### **CROSS-REFERENCE**

This application is a continuation-in-part of U.S. Patent Application No. 08/969,122, entitled A Self-Cleaning Etch Process, @ filed on November 12, 1997, which is incorporated herein by reference.

### **BACKGROUND**

The present invention relates to a method of etching a silicon-containing layer on a substrate.

In the manufacturing of integrated circuits, silicon-containing layers, such as silicon dioxide, silicon nitride, polysilicon, metal silicide, and monocrystalline silicon layers, which are formed on a substrate, and etched to form gates, vias, contact holes, trenches, and/or interconnect lines. In the etching process, a patterned mask layer comprising silicon dioxide, silicon nitride, and/or photoresist, is formed on the substrate using conventional methods, and the exposed portions of the silicon-containing layers on the substrate are etched by microwave or RF energized process gas.

One problem with conventional etching processes arises because it is difficult to etch a surface layer comprising two or more compositionally different regions at the same etch rate. For example, compositionally variant surface layers occur in p-channel and n-channel CMOS transistors fabricated in symmetrical matched pairs, to operate at lower voltages and faster operating speeds. As illustrated in Figure 1a, a set of matched transistors 10a,b comprises adjacent regions in the semiconductor substrate 14 doped with a

WO 00/04213

2

PCT/US99/14922

dopant, such as boron or phosphorous, to form a p-well **12a** and a n-well **12b**. Discrete regions of the p-well **12a** and n-well **12b** are implanted to define the source **16** and drain **18** of the transistors **10a,b**. Next, the surface of the substrate **14** overlying the boundary of the p-well **12a** and n-well **12b** is etched using conventional photolithographic and etching techniques to open a void for an isolation structure **22**. A layer of SiO<sub>2</sub> is formed on the surface of the substrate **14** to create the isolation structure **22** and an overlying gate oxide layer **24**. A layer of polysilicon **28** is grown over the gate oxide layer **24**, and doped with different types of dopant, i.e., n-type or p-type, and different concentrations of dopants to form a gate structure **28a,b** for each transistor **10a,b**. A patterned mask layer **20** is then deposited on the polysilicon layer and it is etched to form the dual gate structures **28a,b**, shown in Figure 1a.

When conventional etching processes are used to etch these types of dual doped polysilicon layers **28**, the different regions **28a,b** are etched at different etch rates. For example, the regions with n-type dopant **28a** are typically etched as much as 20% faster than the regions **28b** with p-type dopant. Also, doped regions are typically etched at much faster rates than undoped regions, or regions in which the implant has not been diffused or activated by annealing the substrate. This difference in etch rates can lead to residues depositing in the more slowly etched regions and/or excess gate oxide **24** loss in the more rapidly etched regions. Furthermore, conventional etching processes also etch features having unacceptably large variations in profile angles (more than 3 degrees) from one region to another region on the substrate **14**. The profile angle is the angle made by a sidewall of the etched features with the plane of the substrate. It is desirable to have an etching process that etches through the compositional variant regions at the substrate surface with uniform etching rates and little or no variations in profile angles of etched features.

WO 00/04213

3

PCT/US99/14922

In one solution, highly chemically reactive etchant gases are used to etch through layers having varying concentration or composition of dopants at a faster and more uniform etch rates. However, the highly reactive etching gas typically provides little or no etching selectivity relative to the resist layer or underlayer, and typically etches through the underlying layer at the same high etch rate. This is particularly common when the underlayer also contains elemental silicon or silicon compounds. For example, when etching through a polysilicon layer that overlies a thin silicon dioxide gate oxide layer, it is necessary to stop the etching process without etching through the underlayer. Thus there is a need for an etching process gas that provides high and uniform etch rates for compositional variant regions in a polysilicon layer without sacrificing the etching selectivity to an underlayer which also contains silicon species.

Another problem arises because it is difficult to clean or remove the thin film of etchant residue that condenses and deposits on the internal surfaces of the chamber, such as the sidewalls, ceiling, and the surfaces of the internal components in the chamber, during the etching process. The composition of the etchant residue depends on the constituents of the process gas, the vaporized material being etched, and the mask layer on the substrate. For example, when tungsten silicide, polysilicon or other silicon-containing layers are etched, silicon-containing gaseous species are vaporized or sputtered to form a large component of the etchant residue deposits. In addition, the mask layer is also partially vaporized to form gaseous hydrocarbon or oxygen species which condense on the internal surfaces of the process chamber. Thus the etchant residue deposits are typically composed of polymeric byproducts containing hydrocarbon species vaporized from the photoresist in the mask layer, process gas species such as fluorine, chlorine, oxygen, or nitrogen; and vaporized silicon-containing species from the polysilicon layer being etched on the substrate. The chemical composition of the etchant residue deposits can

WO 00/04213

4

PCT/US99/14922

also vary considerably across the chamber surface depending upon the composition of the local gaseous environment, the location of gas inlet and exhaust ports, and the geometry of the chamber.

The etchant residue deposits formed on the chamber surfaces are periodically cleaned to prevent contamination of the substrate 14. Typically, after processing of about 25 substrates, an in-situ plasma Adry-clean@ process is used to dry clean the surfaces of the chamber. However, conventional cleaning plasmas that etch the etchant residue deposits contain highly energetic plasma species that rapidly erode the chamber walls and chamber components, and it is expensive to often replace such parts and components. Moreover, after processing of multiple substrates, the etching chamber is opened to the atmosphere and a Awet-cleaning@ process is performed in which an operator uses an acid or solvent to scrub off and dissolve accumulated etchant residue deposits on the internal chamber surfaces. After the wet cleaning step, the chamber is Aseasoned@ by pumping down the chamber to a vacuum environment for 2 to 3 hours to allow moisture and other trapped volatile species to outgas. Thereafter, the etch process to be performed in the chamber, is run for 10 to 15 minutes on a series of dummy wafers until the chamber provides consistent and reproducible etching properties. In the competitive semiconductor industry, the increased cost per substrate and downtime of the chamber, during the dry cleaning, wet cleaning, and seasoning steps is highly undesirable. Also, the cleaning process often provides inconsistent and variable etching properties, because the wet cleaning process is manually performed by an operator.

Thus it is desirable to have an etching process that etches silicon-containing layers having different dopant concentrations at uniform etch rates, and with high etching selectivity to an underlayer. It is especially desirable for the etch process to etch polysilicon layers containing dual-doped or

WO 00/04213

5

PCT/US99/14922

doped/undoped regions with uniform and consistent etch rates. It is also desirable for the etching process to clean-off etchant residue deposits formed on the internal surfaces of the chamber without excessive erosion of the chamber surfaces.

### SUMMARY

The present invention provides a method of etching a polysilicon layer on a substrate. In the method, the substrate is placed in a process chamber, and exposed to an energized process gas comprising a bromine-containing gas, a chlorine-containing gas, an inorganic fluorinated gas, and an oxygen gas.

In another aspect, the process of the present invention is directed to a method for etching a polysilicon layer on a substrate while simultaneously cleaning internal surfaces of a process chamber. The method comprising the steps of, placing the substrate in the process chamber and exposing the substrate and the internal surfaces of the process chamber to an energized process gas. The energized process gas comprising a bromine-containing gas selected from the group consisting of HBr, Br<sub>2</sub>, and CH<sub>3</sub>Br; a chlorine-containing gas selected from the group consisting of Cl<sub>2</sub> and HCl; an inorganic fluorinated gas selected from the group consisting of NF<sub>3</sub>, CF<sub>4</sub>, and SF<sub>6</sub>; and an oxygen gas selected from the group consisting of O<sub>2</sub> and He-O<sub>2</sub>.

In yet another aspect, the process of the present invention is directed to a method for etching a polysilicon layer on a substrate while simultaneously cleaning internal surfaces of a process chamber, in which the polysilicon layer has a first region with a first dopant concentration and a second region with a second dopant concentration. In the method, the polysilicon layer on the substrate and the internal surfaces of the process

WO 00/04213

6

PCT/US99/14922

chamber to an energized process gas comprising a bromine-containing gas selected from the group consisting of HBr, Br<sub>2</sub>, and CH<sub>3</sub>Br; a chlorine-containing gas selected from the group consisting of Cl<sub>2</sub> and HCl; an inorganic fluorinated gas selected from the group consisting of NF<sub>3</sub>, CF<sub>4</sub>, and SF<sub>6</sub>; and an oxygen gas selected from the group consisting of O<sub>2</sub> and He-O<sub>2</sub>. The volumetric flow ratio of the combined volumetric flow rates of the bromine-containing gas, chlorine-containing gas, and oxygen gas, to the volumetric flow rate of the inorganic fluorinated gas is selected to etch the first and second regions at etching rates that differ by less than about 10%.

In still another aspect, the process of the present invention is directed to a multi-stage process for etching a silicon-containing layer on a substrate while simultaneously cleaning internal surfaces of a process chamber.

In the method, the substrate having the silicon-containing layer is placed in the process chamber, and in a first etching stage, an energized first process gas is provided in the process chamber. The first process gas comprising etching gas for etching the silicon-containing layer on the substrate, and cleaning gas for cleaning deposits formed on the internal surfaces of the process chamber during etching of the silicon-containing layer. Next, in a pump-out stage, the flow of the first process gas is stopped and the first process gas is exhausted from the process chamber. Then in a second etching stage, an energized second process gas comprising etching gas for etching the silicon-containing layer is provided in the process chamber, the energized second process gas being substantially absent cleaning gas. Also, the second process gas has a higher selectivity to the underlying gate oxide layer thereby reducing gate oxide loss.

#### DRAWINGS

These and other features, aspects, and advantages of this invention will be better understood from the following drawings and description, which



WO 00/04213

PCT/US99/14922

7

illustrate and describe examples performed according to the process of the present invention.

Figure 1a (prior art) is a schematic cross-section of a substrate comprising symmetric CMOS transistors having a dual gate structure;

Figure 1b (prior art) is a schematic cross-section of a substrate comprising a polysilicon layer with first and second regions having different compositions of dopants, an underlayer of silicon dioxide, and overlying anti-reflective and resist layers;

Figure 2 is a sectional schematic side view of an apparatus suitable for practicing the process of the present invention;

Figure 3 is a graph showing the polysilicon etching rate uniformity for increasing volumetric flow ratio of inorganic fluorinated gas in the process gas;

Figure 4 is a graph showing the etching rate and etching rate uniformity of doped and undoped polysilicon for increasing volumetric flow ratio of inorganic fluorinated gas in the process gas;

Figure 5 is a graph showing the loss of underlying silicon dioxide, and the etching selectivity ratio of etching polysilicon relative to underlying silicon dioxide, for increasing volumetric flow ratio of inorganic fluorinated gas in the process gas;

Figure 6 is a graph showing the etching selectivity ratio of etching the polysilicon layer relative to the overlying resist layer for increasing volumetric flow ratio of inorganic fluorinated gas in the process gas;

WO 00/04213

PCT/US99/14922

8

Figure 7 is a graph showing the reduction in deposition of etchant residue on the internal surfaces of the process chamber (as measured by a quartz crystal microbalance) for increasing volumetric flow ratio of inorganic fluorinated gas in the process gas; and

Figure 8 is a graph showing the change in etchant residue deposition rate on the internal surfaces of the process chamber for increasing volumetric flow ratio of  $\text{CF}_4$  and  $\text{He-O}_2$  in the process gas.

### DESCRIPTION

An apparatus 40 suitable for etching a substrate 45 according to the present invention, as schematically illustrated in Figure 2, comprises an enclosed process chamber 50 for processing the substrate. The particular embodiment of the apparatus 40 shown herein is suitable for processing of semiconductor substrates 45, is provided only to illustrate the invention, and should not be used to limit the scope of the invention. The enclosed chamber 50 has sidewalls 55, a ceiling 60, and a bottom wall 65 fabricated from any one of a variety of materials including metals, ceramics, glasses, polymers, and composite materials. A process zone 70 defined in the process chamber 50 is directly above and surrounds the substrate 45, and comprises a volume of at least about  $10,000 \text{ cm}^3$ , and more preferably about  $10,000$  to about  $50,000 \text{ cm}^3$ . The ceiling 60 can be flat, arcuate, conical, dome-shaped, or multiradius dome shaped. Preferably, the ceiling 60 is dome-shaped to provide a uniform distribution of energized process gas across the entire volume of the process zone 70. This is because the dome-shaped ceiling 60 is further from the substrate 45 than a flat ceiling, thereby reducing dissociated ion recombination losses near the substrate 45 to provide more uniform ion density across the surface of the substrate 45 than a flat ceiling. The dome ceiling 60 can be a

WO 00/04213

9

PCT/US99/14922

flattened dome, conical, truncated conical, cylindrical, or other combination of such shapes, that provides a dome shaped surface above the substrate **45**.

A support **75** having a receiving surface **85** for receiving a substrate **45** thereon is positioned in the process zone **70**. Preferably, the receiving surface **85** comprises grooves **80** that are sized and distributed to hold heat transfer gas such that substantially the entire surface of the substrate **45** is uniformly heated or cooled. Typically, the heat transfer gas contained in the grooves **80** comprises helium or argon which is supplied at a pressure of about 5 to about 30 Torr.

The process gas is introduced into the process chamber **50** through a gas distribution system **85** that includes a process gas supply **90**, a gas flow control valve **95**, and a process gas distributor **100**. The process gas distributor **100** can comprise gas outlets **105** located peripherally around the substrate **45** (as shown), or a showerhead mounted on the ceiling **60** of the chamber **50** with outlets therein (not shown). Spent process gas and etchant byproducts are exhausted from the process chamber **50** through an exhaust system **110** including a vacuum pump **115** (typically a 1000 liter/sec roughing pump) capable of achieving a minimum pressure of about  $10^{-3}$  mTorr in the process chamber **50**. A throttle valve **120** is provided in the exhaust **110** to control the flow of spent process gas and the pressure of process gas in the chamber **50**.

Process gas is energized using a gas energizer **125** to form an energized process gas or a plasma before or after introduction into the process chamber **50**. A suitable gas energizer **125** comprises one or more inductor coils **130** having a circular symmetry with a central axis coincident with the longitudinal vertical axis that extends through the center of the process chamber **50** and perpendicular to the plane of the substrate **45**. Preferably, the inductor coils **130** comprises solenoid coils having from 1 to 10 turns, and more typically

WO 00/04213

PCT/US99/14922

10

from 2 to 6 turns. The arrangement and number of inductor coils 130 is selected to provide the desired product of current and antenna turns  $(d/dt)(N\phi)$  near the ceiling 60 to provide a strong inductive flux linkage with close coupling to the energized process gas and therefore greater ion density in the process zone 70 adjacent to the substrate 45. When the inductor coils 130 are positioned near the dome ceiling 60, the ceiling of the process chamber 50 comprises a dielectric material which is transparent to RF fields, such as a slab of machined silicon dioxide, or tiles of silicon or silicon dioxide bonded to one another to provide a curved shape. Preferably, the inductor coils 130 wrap around the sidewall 55 of the process chamber 50 to form a "flattened" or multiradius dome-shaped that provides increased ion density directly over the substrate 45 because ion density is affected by local ionization near the inductor coil 130, and a multiradius inductor coil is closer to the substrate 45 than a hemispherical coil.

In addition to the inductor coils 130, one or more process electrodes can be used to accelerate the energized process gas ions in the process chamber 50. The process electrodes typically include a cathode electrode 145 in or below the support 75, and a conducting portion of a wall of the process chamber 50, such as the ceiling 60 and/or sidewalls 65, which serves as an anode electrode 140. In a preferred embodiment, the cathode electrode 145 is embedded in a dielectric member 150 positioned on the support 75 to serve as an electrostatic member for electrostatically holding the substrate 45 to the support 75. An electrode voltage supply 155 supplies a RF potential to the cathode electrode 145 that maintains the anode and cathode electrodes 140, 145 at different electrical potentials relative to one another. Alternatively, the gas energizer 125 can also comprise a microwave or other source of ionizing radiation (not shown) capable of energizing the process gas before or after injection into the process chamber 50.

WO 00/04213

11

PCT/US99/14922

The energized process gas in the process zone **70** can also be enhanced using magnetically enhanced reactors, in which a magnetic field generator (not shown), such as a permanent magnet or electromagnetic coils, are used to apply a magnetic field in the process zone **70** to increase the density and uniformity of the energized process gas. Preferably, the magnetic field comprises a rotating magnetic field with the axis of the field rotating parallel to the plane of the substrate **45**, as described in U.S. Patent No. 4,842,683, issued June 27, 1989, which is incorporated herein by reference. The magnetic field in the process chamber **50** should be sufficiently strong to increase the density of the ions formed in the energized process gas, and sufficiently uniform to reduce charge-up damage to features such as CMOS gates. Generally, the magnetic field as measured on the surface of the substrate **45** is less than about 500 Gauss, more typically from about 10 to about 100 Gauss, and most typically from about 10 Gauss to about 30 Gauss.

A process monitoring system, such as an optical endpoint detector **165**, can be used to monitor the process being conducted in the process chamber **50** and determine completion of the etching process for a specific layer. Suitable optical endpoint detectors **165** include detectors based on optical emission, ellipsometry, and interferometry. Optical emission detectors detect the spectral lines in a light spectra emitted by chemically active radicals in the energized process gas to detect changes in chemistry that would indicate the beginning of etching of an underlying layer. Ellipsometers project a light beam at an acute angle to the surface of the substrate **45** to detect a phase shift between portions of the light beam reflected off the top and bottom surfaces of a transparent film on the substrate **45**. An interferometer also reflects a beam of light off the top and the bottom surface of a transparent layer on the substrate **45**, however, an interferometer determines the thickness of a film on the substrate **45**, by measuring the magnitude of constructive or destructive interference between the reflected light beams.

WO 00/04213

12

PCT/US99/14922

During the etching process a thin film of etchant residue condenses or deposits on the internal surfaces of the process chamber 50, such as the sidewalls 55, ceiling 60, and the surfaces of the internal components in the process chamber 50. The composition of the etchant residue deposits depends on the composition of vaporized species and process gas, the substrate material being etched, and the mask or resist layer on the substrate 45. For example, when polysilicon or other silicon-containing layers are etched, silicon-containing gaseous species are vaporized or sputtered to form a large component of the etchant residue deposits. In addition, the photoresist or mask layer is also partially vaporized to form gaseous hydrocarbon or oxygen species. Thus the etchant residue deposits are typically composed of polymeric byproducts containing hydrocarbon species vaporized from the photoresist layer, process gas species such as fluorine, chlorine, oxygen, or nitrogen; and silicon species from the layer being etched on the substrate 45. These etchant residue deposits can flake off during operation of the process chamber 50 and contaminate the substrate 45, or can alter the characteristics of the surfaces on which they are deposited, thereby reducing process uniformity. This is particularly a problem for process chamber surfaces and components comprising ceramic materials, such as aluminum oxide, aluminum nitride, silicon, or silicon oxide, which have highly reactive surface functional groups that are necessary for proper functioning of the process chamber 50.

#### Etching Process

Operation of the process chamber 50 to etch a substrate 45 comprising one or more of silicon-containing layers having different concentrations or compositions of dopant will now be described. The substrate 45 typically comprises a semiconductor material, such as a silicon or gallium arsenide wafer, with a plurality of layers, as shown in Figure 1b. For example, the substrate 45 can include a polysilicon layer 170 comprising first and second

WO 00/04213

13

PCT/US99/14922

regions **180a,b** having different concentrations or compositions of dopants, such as boron or phosphorous. Alternatively, the substrate **45** can comprise a polysilicon layer **170** having a first doped region **180a**, and a second lightly doped or undoped region **180b**, or a region in which the dopant has not been activated by heating the substrate **45** to diffuse the dopant material throughout the region **180b**. In addition, the substrate **45** can also comprise an anti-reflective layer **190** covering the polysilicon layer **170** to reduce reflection during patterning of an overlying photosensitive resist layer **195**. The resist layer **195** is deposited on the substrate **45**, and patterned using conventional photolithographic techniques. The exposed portions of the substrate **45** between patterned features on the resist layer **195** are then etched by the process of the present invention to form features, such as for example, dual-gate structures **28a,b** as shown in Figure 1a.

To perform the process of the present invention, the substrate is placed on the support **75** in the process chamber **50**, and the process chamber evacuated. A process gas is introduced into the process chamber **50** through the process gas distributor **100**, and the throttle valve **120** and/or process gas flow control valve **95** adjusted to maintain pressure in the process chamber **50**. Power is applied to the gas energizer **125** to form an energized process gas to process the substrate **45**. Typically, the power level of the RF current applied to the inductor coils **130**, or source power, determines the amount of dissociated species in the energized process gas. Thus increasing the source power provides more dissociated species and therefore a more rapid albeit a more isotropic etch.

In contrast, increasing the power level of the RF voltage applied to the cathode electrode **145**, or bias power, increases the degree of anisotropic etching by providing a higher kinetic bombardment energy component to the energized process gas. For etching a polysilicon layer **170** comprising regions having different composition or concentrations of dopant, a preferred ratio of source power to bias power  $P_s$  is from about 1:0.1 to about 100:1. More preferably,

WO 00/04213

14

PCT/US99/14922

the process gas is energized by applying a source power level of about 200 to about 2000 Watts, and a bias power level of about 5 to 500 Watts. The frequency of the RF voltage applied to the cathode electrode 145 and/or inductor coils is typically from about 50 KHz to about 60 MHz, and more typically about 13.56 MHz.

A significant advantage of the process of the present invention is that it etches one or more silicon-containing layers that have different concentrations or compositions of dopant at the same etching rate. The process gas comprises an etching gas including a bromine-containing gas, a chlorine-containing gas, an oxygen gas, and an inorganic fluorinated gas. It has been discovered that this combination of gases provides unique and unexpectedly uniform etching rate across a silicon-containing layer having regions with different concentrations or compositions of dopant. Moreover, the process gas composition also significantly reduces the differences in profile angles obtained for features that are etched in regions of the polysilicon layer 170 that have different concentrations of dopant. Furthermore, it has been discovered that the process gas also serves as a cleaning gas that removes etchant residue deposits from the internal surfaces of the process chamber 50.

The bromine-containing gas of the process gas enhances the rate of etching of a silicon-containing layer, such as the polysilicon layer 170, while simultaneously reducing the rate of etching of the resist layer 195 thereby enhancing the etching selectivity ratio of the silicon-containing layer 170 to the resist layer 195. It is believed the bromine in the bromine-containing gas reacts with Si in the silicon containing layer to form a sidewall passivation layer and does not react with resist as aggressively as  $\text{Cl}_2$  thereby reducing erosion of the resist layer 195. The bromine-containing gas can comprise HBr, or can comprise other bromine-containing gases that are equivalent to HBr, for example,  $\text{Br}_2$ ,



WO 00/04213

15

PCT/US99/14922

CH<sub>3</sub>Br, and mixtures thereof. For etching polysilicon, HBr is preferred because it provides more sidewall passivation deposits for more anisotropic etching.

The chlorine-containing gas functions as the main etchant for etching the silicon-containing layer 170 on the substrate 45. The chlorine-containing gas is ionized to form atomic chlorine and chlorine-containing species that etch the silicon-containing layer 170 on the substrate 45. For example, silicon in the polysilicon layer 170 can be etched by chlorine-containing ions and neutrals to form volatile SiCl<sub>x</sub> species that are exhausted from the process chamber 50. The chlorine-containing gas can comprise Cl<sub>2</sub>, or can comprise other chlorine-containing gases that are equivalent to chlorine, for example, HCl, BCl<sub>3</sub>, and mixtures thereof. For etching polysilicon, Cl<sub>2</sub> is preferred because it has a high etch rate for etching silicon.

The oxygen gas is provided to increase the etching selectivity ratio of etching polysilicon relative to silicon dioxide. It is believed that the oxygen gas ionizes to form ions and excited radicals of atomic oxygen and oxygen-containing species that enhance the rate of etching of the polysilicon layer 170, while simultaneously reducing the rate of etching of the silicon dioxide layer 175. The oxygen gas can also comprise an oxygen compound which includes inert gases, such as for example, helium, xenon, argon, or krypton. For etching polysilicon, He-O<sub>2</sub> gas is preferred because the helium gas serves as a diluent gas that reduces the residence time of the process gas in the process chamber 50. In addition, He-O<sub>2</sub> gas serves to add very small volumes of oxygen to the process gas.

The volumetric flow ratios of chlorine-containing gas to bromine-containing gas are selected to etch the silicon-containing layer faster than the resist layer 195 and the silicon dioxide layer 175. Preferably, the silicon-containing layer is etched at an etch rate of at least about 2000 Å/min, and more

WO 00/04213

16

PCT/US99/14922

preferably, the silicon-containing layer is etched at an etch rate of about 3000 Å/min an etching selectivity ratio of at least about 2:1. The volumetric flow ratio of chlorine-containing gas to bromine-containing gas is also selected to provide anisotropically etched features having sidewalls with smooth surfaces that form angles of at least about 88° with a plane of the substrate 45, and more preferable angles of from about 89° to about 90°. If the volumetric flow rate of chlorine-containing gas is too high, or the total volumetric flow rate of other gases too low, the etch rate is too rapid. A rapid etch rate exceeding the rate at which passivation deposits are formed results in an isotropic etch that provides features having undercut sidewall profiles. Preferably, the volumetric flow ratio of chlorine-containing gas to bromine-containing gas is from about 1:5 to about 5:1, and more preferably about 1:1.

The volumetric flow ratio of oxygen gas to chlorine-containing gas and bromine-containing gas is selected to provide a substantially anisotropic etch of the silicon-containing layer 170, and to provide good selectivity relative to silicon dioxide when etching a polysilicon layer 170. The flow of oxygen gas should be sufficient to prevent the accumulation of passivating deposits from reducing the etch rate. However, excessively high flow rates of oxygen gas can also cause more isotropic etching of the substrate 45 by removing the passivating deposits formed on the etched features too quickly. Thus, the flow rate of the oxygen gas is maintained lower than the flow rate of the chlorine-containing gas to provide sufficient chlorine-containing species to rapidly etch the substrate 45, while providing a high polysilicon to silicon dioxide etching selectivity and more anisotropic etching. Preferably, when a premixed mixture of He-O<sub>2</sub> having about 3 parts helium to 1 part oxygen is used, the volumetric flow ratio of He-O<sub>2</sub> gas to chlorine-containing gas is at least about 1:20, and more preferably from about 1:3 to about 1:13.

WO 00/04213

17

PCT/US99/14922

The ratio of the inorganic fluorinated gas to the other gas constituents controls many of the unexpected features of the present process. For example, the volumetric flow ratio of the inorganic fluorinated gas to the combined flow rates of the bromine-containing gas, chlorine-containing gas, and oxygen gas, controls the rate of etching regions on the silicon-containing layer that have different compositions and concentrations of dopants to provide etching rates that differ by less than 10%, and more preferably, are substantially the same. The addition of inorganic fluorinated gas significantly enhances the control of the profile angle of the etched features of the polysilicon layer 170. The ratio of volumetric flow rate of the inorganic fluorinated gas to the combined flow rates of other process gases also controls the rate of removal of etchant residue, and can remove residues generated from processing 2000 to 3000 substrates 45, without stopping the etching process for a wet clean operation. It has been discovered that a suitable volumetric flow ratio of the combined volumetric flow rates of the bromine-containing gas, chlorine-containing gas, and oxygen gas, to the volumetric flow rate of the inorganic fluorinated gas is from about 4:1 to about 20:1 and more preferably is from about 5:1 to about 10:1.

The process gas composition described above has been discovered to provide numerous advantages over process gas compositions for etching silicon-containing layers. The process gas composition of the present invention provides uniform and consistent etching rates for etching a silicon-containing layer having regions of different concentration/composition of dopant, providing etching rate variations of as low as 10% is in contrast to conventional gas composition that typically provide etching rates more than 25%. In addition, this process gas composition provides etched features having profile angles of 88 to 90° for the etched features of both the doped and undoped polysilicon. The profile angle, i.e., the angle between the sidewall of the etched feature and the plane of the substrate 45, is ideally about 90° to provide features having straight and substantially perpendicular sidewalls. Features having straight

WO 00/04213

18

PCT/US99/14922

sidewalls can be formed closer together leading to higher circuit densities and faster operating speeds. However, conventional etching processes often result in a profile difference of greater than 3 $\times$  between doped and undoped regions or n-doped and p-doped regions. Moreover, the deposition of etchant residue on the internal surfaces of the process chamber 50 drops from a rate of over 30  $\text{\AA}/\text{min}$  with conventional etching process gas compositions, to a removal rate of over 40  $\text{\AA}/\text{min}$ .

In a preferred embodiment of the present process, multiple stages are used to completely etch through a polysilicon layer 170 having different concentrations or compositions of dopant without etching through the thin underlying silicon dioxide layer 175. In addition, inorganic fluorinated gas is introduced in at least one of the stages to remove the etchant residue deposits on the process chamber surfaces. In a first or main etching stage, most of the thickness of the polysilicon layer 170 that are exposed through openings in the resist layer 195 is etched. The process gas comprises an etching gas comprising  $\text{Cl}_2$ ,  $\text{HBr}$ , and  $\text{He-O}_2$ , and an inorganic fluorinated cleaning gas, such as  $\text{CF}_4$ , or  $\text{NF}_3$ , in volumetric flow ratios suitable for etching the polysilicon layer 170 with a high etch rate and a high selectivity ratio relative to the resist layer 195. A suitable volumetric flow ratio of inorganic fluorinated gas to total volumetric flow ratio is about 0.15:1. The source power applied to the inductor coils 130 is about 500 watts, and the bias power applied to the cathode electrode 145 is about 80 watts. The process chamber pressure is about 4 mTorr, and the substrate is maintained at a temperature of about 50 $^\circ\text{C}$  by supplying helium to the grooves 80 at a pressure of about 8 Torr. Preferably, the main etch stage provides a polysilicon etch rate of from about 1800  $\text{\AA}/\text{min}$  to about 2500  $\text{\AA}/\text{min}$ , and an etching selectivity ratio relative to silicon dioxide of from about 3:1 to about 7:1.

WO 00/04213

PCT/US99/14922

19

The main etch stage is stopped by the optical endpoint detector 165, immediately before the polysilicon layer 170 is completely etched through. A suitable endpoint detection method is optical emission analysis in which an emission spectra of the energized process gas in the process chamber 50 is analyzed to determine a change in chemical composition that corresponds to a change in the chemical composition of the layer being etched, as taught in U.S. Patent No. 4,328,068 which is incorporated herein by reference.

A pump-out step is performed after the main etch stage is stopped, to exhaust the process gas of the main etch stage from the process chamber 50, and in particular to remove substantially all of the inorganic fluorinated gas. The inorganic fluorinated gas is a chemically aggressive gas that would rapidly etch through the thin underlying silicon dioxide layer 175, and its removal is needed to preserve the silicon dioxide layer 175. In the pump-out step, the process chamber 50 is pumped down to a pressure sufficiently low, and for a sufficient time to ensure that substantially all of the inorganic fluorinated gas is removed from the process zone 70. Preferably, the chamber 50 is evacuated to a pressure of from about 0.5 mTorr to about 1 mTorr. More preferably the process chamber 50 is maintained at a pressure of less than about 0.5 mTorr for from about 5 to about 15 seconds, to ensure that substantially all of the inorganic fluorinated gas is removed from the process zone 70. Optionally, a low flow of an inert purge gas, such as nitrogen, may be introduced during the pump-out stage to dilute any remaining inorganic fluorinated gas in the chamber 50 and to prevent back-streaming of oil from the vacuum pump 115. A suitable flow rate is from about 50 to about 100 sccm.

After the pump-out step, a second or overetch stage is performed in which the portion of the polysilicon layer remaining on the substrate is etched. In the overetch stage, a second process gas, which is substantially absent inorganic fluorinated gas, is energized by the gas energizer 125. For example,

WO 00/04213

20

PCT/US99/14922

the overetch stage can comprise a process gas including 160 sccm HBr and 10 sccm He-O<sub>2</sub>; a process chamber pressure of 50 mTorr; a source power level of 1000 Watts; and a RF bias power level of 100 Watts. More preferably, the process gas composition of the overetch stage is selected to provide a polysilicon etch rate of from about 1500 Å/min to about 3000 Å/min, and an etching selectivity ratio relative to silicon dioxide of from about 50:1 to about 150:1.

In addition to uniform etching through polysilicon layers 170 having different concentrations/compositions of dopant, the etching process of the present invention has been found to clean and remove etchant residue deposited on surfaces of the process chamber 50 during the etching process, irrespective of the thickness or chemical stoichiometry of the etchant residue deposits. Prior art etching processes required cleaning and conditioning of the process chamber 50 after processing of only 200 to 300 substrates 45, because amount of etchant residue deposits on the chamber surfaces, after processing this number of substrates 45. Build-up of etchant deposits resulted in flaking off and contamination of the substrate 45. Also, prior art cleaning processes, particularly those performed by an operator, often fail to uniformly clean and remove the etchant residue deposits formed on process chamber surfaces. Furthermore, the activated cleaning gas can be used to efficiently clean the process chamber 50 in-situ during etching of substrates 45, rather than stopping processing to wet clean the process chamber walls and components, thereby increasing etching throughput and further reducing costs per substrate 45. In contrast, the process of the present invention removes the etchant residue deposits formed across substantially all of the process chamber surfaces, to reduce substrate contamination and increase yields. A process gas comprising the cleaning gas also results in much less erosive damage to the process chamber 50 compared to conventional in-situ plasma cleaning steps, because of the reduced energy levels of the energized process gas in the process chamber

WO 00/04213

PCT/US99/14922

21

50. This was difficult to accomplish in prior art processes, in which the high powered plasmas needed to remove the accumulated etchant residue deposits often resulted in extensive erosion of chamber surfaces and components. By reducing the need to replace process chamber components, the cost of operating the process chamber 50 and the cost per substrate 45 are significantly reduced. The etching process is expected to increase process chamber 50 lifetimes by a factor of at least 2.

### EXAMPLES

The following examples illustrate use of the present invention for etching polysilicon layers 170 on semiconductor substrates 45 and cleaning etchant residue deposits off the internal surfaces of the process chamber 50. However, the apparatus 40 and method can be used in other applications as would be apparent to those skilled in the art, and the scope of the present invention should not be limited to the illustrative examples provided herein.

In these examples, the process of the present invention was used to etch a polysilicon layer 170 on a substrate 45 to expose a thin underlayer of silicon dioxide 175. The polysilicon layer 170 comprised first and second regions 180a,b having different concentrations or compositions of dopants, including undoped regions or regions in which the dopant has not been activated. The substrates 45 were silicon wafers having a diameter of 200 mm, and comprising a polysilicon layer 170 2500 Å thick over a underlayer of silicon dioxide 175 45 Å thick, and an overlying BARC anti-reflective layer 190 700 Å thick. A resist layer 195 comprising an 8000 Å thick layer of a deep ultra-violet DUV resist was deposited on the anti-reflective layer 190 and patterned using conventional techniques. The substrates 45 were etched according to the process of the present invention, and after the etching process, measurements were made to determine the thickness of the polysilicon layer 170 removed, the thickness of

WO 00/04213

22

PCT/US99/14922

the silicon dioxide layer 175 remaining, the etching rate, the etching uniformity, and the etching selectivity of the polysilicon layer 170 relative to the overlying resist layer 195 and underlaying silicon dioxide layer 175. The uniformity of the doped and undoped polysilicon etching rates was determined from  $(\text{maximum etch rate} - \text{minimum etch rate}) / (2 \times \text{average etch rate}) \times 100\%$ . The etching rates were measured from by partially etching the polysilicon layer 170 and measuring the remaining polysilicon with an interferometer, such as a Prometrix UV 1050.

In addition, the process gas composition was tailored to clean or prevent deposition of excessive etchant residue on the internal surfaces of the process chamber 50. A quartz crystal microbalance (QCM) 200 was used to determine the amount of etchant residue deposits and other process gas byproducts that were being deposited on the process chamber surface during the etching process. The quartz crystal microbalance 200 comprised a piezoelectric plate that changed in capacitance when a film of etchant residue is deposited on the plate. The microbalance 200 was mounted on an internal surface of the process chamber 50, such as a sidewall 55, and its leads connected to a computer outside the process chamber 50.

In these examples, the process gas composition for etching the polysilicon layer 170 was changed by adding increasing amounts of inorganic fluorinated gas, such as  $\text{CF}_4$ , in the main polysilicon etching step. After etching the BARC layer 190, two successive polysilicon etching stages were used to etch the polysilicon layer 170. The first or main etching stage used a more chemically reactive process gas containing inorganic fluorinated cleaning gas, such as  $\text{CF}_4$ , and in the second stage, the process gas was substantially absent the inorganic fluorinated gas to provide a less chemically reactive etching process.



WO 00/04213

23

PCT/US99/14922

The constant values of process conditions for the main etching stage, included a process gas comprising 60 sccm  $\text{Cl}_2$ , 100 HBr sccm, and 16 sccm  $\text{He-O}_2$ . The volume%  $\text{CF}_4$  gas was varied between 0%, 13.5%, 19% and 26.3% of the total gas flow. The pressure in the process chamber 50 was maintained at 4 mTorr, the RF source power applied to the inductor coil 130 was 475 Watts, and the RF bias power applied to the cathode electrode 145 was 80 watts. During the process, the substrate 45 was cooled to a temperature of  $50^\circ\text{C}$  using a flow of helium on the backside of the substrate 45 maintained at a pressure of about 8 Torr.

The process gas compositions provided uniform and consistent etching rates for etching the polysilicon layer 170 across the entire substrate surface. For example, Figure 3 shows the polysilicon etching rate uniformity (at one sigma standard deviation) for increasing volumetric flow ratio concentration of inorganic fluorinated gas in the process gas composition. As the volumetric flow ratio of  $\text{CF}_4$  increased from 0 to 19%, the uniformity of etching the polysilicon layer 170 gradually decreased from 1.2 to 0.4, and thereafter, when the  $\text{CF}_4$  concentration was 24 volume% the polysilicon etching rate uniformity increased to about 0.6. This etching uniformity factor is 1 to 2 times better than that provided by conventional etching processes.

Figure 4 shows the etching rates of doped polysilicon and undoped polysilicon, and the ratio of the etching rate of doped and undoped polysilicon, for increasing volumetric flow ratio of inorganic fluorinated gas. The etching rate for the doped polysilicon gradually decreased from about 2600  $\text{\AA}/\text{min}$  at 0 volume%  $\text{CF}_4$  to about 2300  $\text{\AA}/\text{min}$  at a 13.5 volume%  $\text{CF}_4$ , and thereafter remained constant for increasing  $\text{CF}_4$  concentrations. Surprisingly, in contrast to the expectation from the change of etching rates of the doped polysilicon, the etching rate for the undoped polysilicon initially decreased from about 2100  $\text{\AA}/\text{min}$  at 0 volume%  $\text{CF}_4$  to about 1900  $\text{\AA}/\text{min}$  at a 13.5 volume%  $\text{CF}_4$ , but

WO 00/04213

24

PCT/US99/14922

thereafter, gradually increased back to 2100  $\text{cm}^3/\text{min}$  for increasing  $\text{CF}_4$  concentrations of up to 24 volume%.

Prior art etching processes resulted in significant variations in etching rates of doped and undoped polysilicon across the surface of the substrate 45. In contrast, a process gas composition according to the present invention provides unexpectedly uniform and high etching rates for etching both the doped and undoped polysilicon across the surface of the substrate 45 because the etching rate for the doped polysilicon decreases as the etching rate of the undoped polysilicon is increased. As shown in Figure 4, this effect causes the ratio (or uniformity) of the doped polysilicon etch rate to the undoped polysilicon etch rate to drop down from 1.25 to about 1.1 for as the volume% of  $\text{CF}_4$  is increased from 0 to 24 volume%. The uniformity of etching rates for the doped and undoped polysilicon layer 170 of as low as 1.1 is in contrast to conventional etching rate variations that are typically greater than 1.25, as demonstrated herein.

The process gas composition was also selected to provide a high etching selectivity ratio for etching the polysilicon layer 170 relative to the underlying silicon dioxide layer 175. The high etching selectivity ratio of the polysilicon layer 170 to the underlying silicon dioxide layer 175 reduces the possibility of overetching into the underlying silicon dioxide layer 175 after etching through the overlying polysilicon layer 170. A high etching selectivity ratio is desirable to prevent overetching and Abreakthrough@ into the underlying electrically insulating silicon dioxide layer 175. Figure 5 is a graph showing the loss of underlying silicon dioxide, and the etching selectivity ratio of etching polysilicon relative to underlying silicon dioxide, for increasing volumetric flow ratio of inorganic fluorinated gas to total gas. The loss of thickness of the silicon dioxide layer 175 increased from 5 to about 32  $\text{\AA}$  with increasing volumetric flow ratio of  $\text{CF}_4$ , as shown in Figure 5, resulted because the fluorine content of the

WO 00/04213

25

PCT/US99/14922

CF<sub>4</sub> gas etches away silicon dioxide to form volatile SiFx gases. This reduces the etching selectivity ratio for etching polysilicon relative to silicon dioxide from about 14 to about 4, with the addition of 0 to 24 volume%, respectively, of inorganic fluorinated gas consisting of CF<sub>4</sub>. The loss in etching selectivity ratio is undesirable because the underlying silicon dioxide layer 175, which is very thin in the newer integrated circuits, can be rapidly etched away as soon as the overlying polysilicon layer 170 is etched through.

It is also generally desirable to have a high etching selectivity for etching the polysilicon layer 170 relative to the resist layer 195, to avoid etching through the resist layer 195 before the polysilicon layer 170 is etched through. Figure 6 shows the etching selectivity ratio for etching the polysilicon layer 170 relative to the overlying resist layer 195 for increasing volumetric flow ratio of inorganic fluorinated gas. The etching selectivity for etching the polysilicon layer 170 relative to the resist layer 195 generally increases a small amount from about 1.4 to about 1.6 with the addition of 0 to 24 volume%, respectively, of inorganic fluorinated gas such as CF<sub>4</sub>. Thus the resist etching selectivity ratio is not adversely affected by the addition of the CF<sub>4</sub> gas.

Figure 7 is a graph showing the reduction in deposition of etchant residue on the internal surfaces of the process chamber 50 (as measured by a quartz crystal microbalance 200) for increasing volumetric flow ratio of inorganic fluorinated gas. This graph demonstrates the substantial and unexpected cleaning of the etchant residue deposits on the internal chamber surfaces that is provided by the addition of the inorganic fluorinated gas to the process gas. An increase of CF<sub>4</sub> gas flow from 0 volume% to 24 volume% reduces the normalized rate of deposition of etchant residue deposits on the internal surfaces of the process chamber 50 from over 30 Å/min to under -80 Å/min. The negative values indicate that the etchant residue deposits were actually being

WO 00/04213

26

PCT/US99/14922

removed from the microbalance 200 in the process instead of being deposited on the microbalance.

Table I lists the values of the normalized etchant residue deposition rates and polysilicon to silicon dioxide etching selectivity ratios for increasing  $\text{CF}_4$  gas content in the process gas composition. As demonstrated by the graphs, the higher the  $\text{CF}_4$  gas content, the better or lower is the normalized etchant residue deposition rates, and the lower the etching uniformity for etching doped to undoped polysilicon. In fact, at a  $\text{CF}_4$  volume% flow of 24.3% of total gas flow, the normalized etchant residue deposition rate is -80 indicating etchant residue is actually removed, and the doped/undoped polysilicon etching uniformity drops to as low as 1.1.

TABLE I					
Volume% $\text{CF}_4$	Normalized Etch Residue Deposition Rate ( $\text{\AA}/\text{min}$ )	Doped	Polysilicon	Undoped Polysilicon Etch Rate ( $\text{\AA}/\text{min}$ )	Doped/Undoped Polysilicon Etching Uniformity ( $\text{\AA}/\text{min}$ )
		Etch Rate ( $\text{\AA}/\text{min}$ )	Etching Uniformity (1 $\sigma$ )		
0	32	2612	1.22	2088	1.25
13.5	-39	2304	0.85	1937	1.19
19	-61	2311	0.48	1963	1.18
24.3	-80	2316	0.65	2126	1.1

The interaction of the inorganic fluorinated gas constituent with the other gas constituents of the process gas composition is also unexpected. For example, Figure 8 shows the change in etchant residue deposition rates on the internal surfaces of the process chamber 50 for increasing volume percentage of

WO 00/04213

27

PCT/US99/14922

CF<sub>4</sub> and He-O<sub>2</sub>. Generally, with a CF<sub>4</sub> gas content increase from 13.5 volume% to 24 volume%, the etchant residue deposition rates on the internal surfaces of the process chamber 50 is reduced from about -39 Å/min to about -80 Å/min. An increase of He-O<sub>2</sub> gas content from 16 to 25 sccm, reduces the rate of etchant residue deposition on the internal surfaces of the process chamber 50. However, a further increase of He-O<sub>2</sub> gas content from 25 to 40 sccm increases the rate of etchant residue deposition on the internal surfaces of the process chamber 50, which is undesirable. It is believed that the increase in etch residue deposition on the surfaces of the process chamber 50 with an increase in He-O<sub>2</sub> gas content, results because the O<sub>2</sub> in the He-O<sub>2</sub> reacts with silicon-containing materials and forms SiO<sub>2</sub> deposits on the chamber walls.

Table II lists the values of the normalized etch residue deposition rates and polysilicon to silicon dioxide etching selectivity ratios for increasing CF<sub>4</sub> and He-O<sub>2</sub> gas content in the process gas composition. Of these results, a He-O<sub>2</sub> gas content of 25 sccm and a CF<sub>4</sub> gas content of about 25 sccm, are preferred because these flow rates provide a balance between the polysilicon to silicon dioxide etching selectivity ratio and the rate of deposition of etch residue on the internal chamber surfaces. The volumetric flow ratios of oxygen-containing gas to inorganic fluorinated gas are selected so that the energized process gas cleans off substantially all etch residue deposits formed on internal surfaces of the process chamber, and has high selectivity of polysilicon to silicon dioxide. Preferably, the volumetric flow ratio of the oxygen gas, to the volumetric flow rate of the inorganic fluorinated gas is from about 1:1 to about 1:10, and more preferably about 1:1.5.

WO 00/04213

28

PCT/US99/14922

TABLE II				
	13.5 Volume% CF <sub>4</sub>		24 Volume% CF <sub>4</sub>	
He-O <sub>2</sub> Flow Rate (sccm)	Normalized Etch Residue Deposition Rate	Polysilicon to Silicon Dioxide Etching Selectivity Ratio	Normalized Etch Residue Deposition Rate	Polysilicon to Silicon Dioxide Etching Selectivity Ratio
16	-39	5	-80	3.65
25	-48	6.65	-108	5.06
40	0	8.4	-86	6.2

Referring to Table III, this example illustrates a process for etching a polysilicon layer 170 on the substrate 45 using multiple stages, that include at least three separate stages, comprising an initial stage in which the anti-reflective BARC layer 190 is etched, a main polysilicon etching stage, and an overetch polysilicon etching stage. In the first stage, the BARC layer on the substrate 45 was etched by introducing a process gas comprising 40 sccm Cl<sub>2</sub> and 20 sccm O<sub>2</sub>, into the process chamber 50, and forming an energized process gas by applying a RF source power of 300 Watts to the inductor coil and a RF bias power of 40 Watts to the cathode electrode 145. A pressure of 2mTorr was maintained in the process chamber 50. During the process, the substrate 45 was cooled to a temperature of 50°C by flowing helium on the backside of the substrate 45 at a pressure of about 8 Torr. An optical emission end point detector 165 was used to determine completion of etching of the BARC layer 190.

WO 00/04213

29

PCT/US99/14922

TABLE III				
Process Variable		Step 1 BARC Etch	Step 2 Polysilicon Main Etch	Step 3 Polysilicon Overetch
Cl <sub>2</sub>	sccm	40	60	0
O <sub>2</sub>	sccm	20	0	0
HBr	sccm	0	100	100
He-O <sub>2</sub>	sccm	0	16	6
CF <sub>4</sub>	sccm	0	25	0
Source Power	Watt	300	475	750
Bias Power	Watt	40	80	100
Pressure	mTorr	2	4	50
Temperature	°C	50	50	50
Backside Helium	Torr	8	8	8

After etching the BARC layer 190, the two successive polysilicon etching stages, namely the main etch and the overetch, were used to etch the polysilicon layer 170. The first or main etching stage used a more chemically reactive process gas containing inorganic fluorinated cleaning gas, such as CF<sub>4</sub>, and in the second stage, the process gas was substantially absent the inorganic fluorinated gas to provide a less chemically reactive etching process. In the main etching stage, the process gas comprised 60 sccm Cl<sub>2</sub>, 100 HBr sccm, 16 sccm He-O<sub>2</sub>, and 25 sccm of CF<sub>4</sub>, which provides a volumetric flow ratio of the combined flow rates of bromine-containing gas, chlorine-containing gas, and oxygen-containing gas to the flow rate of inorganic fluorinated gas of about 7:1. After the main etching stage, the optical emission endpoint detector 165 was

WO 00/04213

30

PCT/US99/14922

used to detect and stop the etching process without etching through the underlying silicon dioxide layer 175 on the substrate 45.

In between the main etch stage and the overetch stage, a pump-out step was performed in which the process chamber 50 was exhausted of process gas by pumping down the chamber 50. In this step, the throttle valve 120 was maintained fully open for about 10 seconds, to achieve a pressure of less than 0.5 mTorr. The pump-out step was performed to exhaust and remove substantially all the residual inorganic fluorinated gas in the process zone 70 of the process chamber 50. The pump-out step significantly enhanced the etching selectivity of etching the polysilicon layer 170 to underlying silicon dioxide layer 175 by removing all of the aggressive inorganic fluorinated gas prior to the silicon dioxide layer 175 being exposed.

After the chamber 50 was pumped down, the overetch stage was performed to etch through the residual portion of the polysilicon layer 170. In this stage, the inorganic fluorinated gas content was entirely eliminated, to obtain slower and more controllable etching rates. In this stage, the process gas comprised 100 sccm HBr and 16 sccm He-O<sub>2</sub>; the chamber pressure was 50 mTorr; the source power level was 750 Watts; and the RF bias power level was 100 Watts.

In this example, the remaining silicon dioxide gate oxide layer 175 had a thickness of about 3.3 nm (33 Å) below both the doped and undoped polysilicon regions. It is desirable to stop the etching process on the gate oxide layer because the active source and drain regions underlying the gate oxide layer 175 can undergo charge damage and lattice structural damage upon exposure to the energetic ions of the energized process gas.



WO 00/04213

31

PCT/US99/14922

In addition, this example provided etched features having profile angles of 87 to 88° for both the etched features of doped polysilicon as well as the etched features of undoped polysilicon, and in both the dense and isolated regions of the substrate 45. The profile angle, i.e., the angle between the sidewall of the etched feature and the plane of the substrate 45, is ideally about 90° to provide features having straight and substantially perpendicular sidewalls. Features having straight sidewalls can be formed closer leading to higher circuit densities and faster operating speeds.

The variations in critical dimensions for the etched features on the substrate 45 was also measured. Critical dimensions are predefined and desirable dimensions of the etched features needed to provide the desired electrical properties of the etched features in the design of integrated circuits. The critical dimensions are typically measured as a ratio or difference between the width  $W_r$  of the resist features 195 and the width  $W_e$  of the etched features. The closer the width of the etched feature to that of the resist feature the more predictable and reliable are the electrical properties of the etched feature. In newer integrated circuits, the line widths of interconnect lines and diameters of contact plugs are increasingly becoming smaller than 0.25 microns, to accommodate higher circuit densities. Because the electrical resistance of these features is proportional to the cross-sectional area of the etched features, it is important to maintain consistent and uniform dimensions without variations from feature to feature. Tapering cross-sections and cross-sectional profiles that vary as a function of the spacing of the features are no longer acceptable in these integrated circuits. In the present example, the densely packed feature portion of the substrate 45 (which had closely spaced etched features), exhibited a critical dimension loss of about -0.005 microns, and the isolated regions showed a critical dimension loss of about -0.003 microns.

WO 00/04213

32

PCT/US99/14922

In addition, prior art etching processes required cleaning and conditioning of the process chamber 50 to reduce contamination levels that resulted from excessive deposition of etch residue deposits on the internal chamber surfaces, after processing a large number of substrates 45. In contrast, the present etching and simultaneous cleaning process provided consistently high and uniform polysilicon etching rates of 3000 Å/min and a variation in etching rate of about 1.7%, during continuous etching of 3000 substrates without requiring a separate cleaning process step. The process has been found to uniformly remove etch residues, irrespective of their thickness or chemical stoichiometry; whereas prior art cleaning processes often fail to uniformly remove the etch residue deposits formed on chamber surfaces.

This example illustrates a process for etching a polysilicon layer 170 using a process gas comprising inorganic fluorinated gas consisting of  $\text{NF}_3$ . Three separate stages, including an initial stage in which the anti-reflective 190 BARC layer is etched, a main polysilicon etching stage, and an overetch polysilicon etching stage, were used, as listed in Table IV.

As in the prior example, in between the main etch stage and the overetch stage, a pump-out step was performed in which the process chamber 50 was exhausted of process gas by pumping down the process chamber 50. In this step, the throttle valve 120 was maintained fully open for about 10 seconds, to achieve a pressure of less than 0.5 mTorr. The pump-out step was performed to exhaust and remove substantially all the residual content of inorganic fluorinated gas in the process chamber 50. The pump-out step significantly enhanced the etching selectivity of the polysilicon layer 170 to underlying silicon dioxide layer 175. Only after the process chamber 50 was pumped out, was the overetch stage performed to etch through the residual portion of the polysilicon layer 175.

WO 00/04213

33

PCT/US99/14922

TABLE IV				
Process Variable		<u>Step 1</u> BARC Etch	<u>Step 2</u> Polysilicon Main Etch	<u>Step 3</u> Polysilicon Overetch
Cl <sub>2</sub>	sccm	40	60	0
O <sub>2</sub>	sccm	20	16	0
HBr	sccm	0	100	100
He-O <sub>2</sub>	sccm	0	16	6
NF <sub>3</sub>	sccm	0	25	0
Source Power	Watt	300	475	750
Bias Power	Watt	40	80	100
Pressure	mTorr	2	4	50
Temperature	°C	50	50	50
Backside Helium	Torr	8	8	8

In this example the remaining silicon dioxide gate oxide layer 175 had a thickness of about 3.4 nm (34 Å) below both the doped and undoped polysilicon regions, and provided etched features having profile angles of 87 to 88°. In addition, the normalized rate of deposition of etch residue on the chamber walls, as measure by the microbalance, was about -64 Å/minute as compared to -9 Å/minute for the equivalent flow rate of CF<sub>4</sub> gas in the process gas composition. Thus the NF<sub>3</sub> gas composition provided better cleaning results than the CF<sub>4</sub> gas composition. In addition, the NF<sub>3</sub> based gas composition provided better etching selectivity for etching polysilicon relative to silicon dioxide, by providing an etching selectivity ratio of 8:1 as compared to 5:1 for CF<sub>4</sub> gas.

WO 00/04213

34

PCT/US99/14922

The present invention has been described with reference to certain preferred versions thereof; however, other versions are possible. For example, the treatment and cleaning process of the present invention can be used for treating chambers for other applications, as would be apparent to one of ordinary skill. For example, the process can be applied, as would be apparent to one of ordinary skill in the art, to treat sputtering chambers, ion implantation chambers, or deposition chambers, or in combination with other cleaning processes. Therefore, the spirit and scope of the appended claims should not be limited to the description of the preferred versions contained herein.

WO 00/04213

35

PCT/US99/14922

**What is claimed is:**

1. A method of etching a polysilicon layer on a substrate, the method comprising the steps of:
  - (a placing the substrate in a process chamber, the substrate having a polysilicon layer; and
  - (b exposing the substrate to an energized process gas comprising a bromine-containing gas, a chlorine-containing gas, an inorganic fluorinated gas, and an oxygen gas.
2. A method according to claim 1 wherein the volumetric flow ratio of the bromine-containing gas, chlorine-containing gas, inorganic fluorinated gas, and oxygen gas is selected so that the energized process gas etches regions having different concentrations of dopant in the polysilicon layer at substantially the same etching rate.
3. A method according to claim 1 wherein the volumetric flow ratio of the bromine-containing gas, chlorine-containing gas, inorganic fluorinated gas, and oxygen gas is selected so that the energized process gas cleans off etch residue deposits formed on internal surfaces of the process chamber during etching of the polysilicon layer.
4. A method according to claim 3 wherein the volumetric flow ratio of the combined volumetric flow rates of the bromine-containing gas, chlorine-containing gas, and oxygen gas, to the volumetric flow rate of the inorganic fluorinated gas is from about 4:1 to about 20:1.
5. A method according to claim 1 wherein the bromine-containing gas comprises one or more of HBr, Br<sub>2</sub>, or CH<sub>3</sub>Br.

WO 00/04213

36

PCT/US99/14922

6. A method according to claim 1 wherein the chlorine-containing gas comprises one or more of  $\text{Cl}_2$  or  $\text{HCl}$ .

7. A method according to claim 1 wherein the inorganic fluorinated gas comprises one or more of  $\text{NF}_3$ ,  $\text{CF}_4$ , or  $\text{SF}_6$ .

8. A method according to claim 1 wherein the oxygen gas comprises one or more of  $\text{O}_2$  or  $\text{He-O}_2$ .

9. A method according to claim 1 wherein the energized process gas comprises  $\text{HBr}$ ,  $\text{Cl}_2$ ,  $\text{He-O}_2$ , and one or more of  $\text{NF}_3$ ,  $\text{CF}_4$ , or  $\text{SF}_6$ .

10. A method according to claim 1 wherein the energized process gas consists essentially of  $\text{HBr}$ ,  $\text{Cl}_2$ ,  $\text{He-O}_2$ , and  $\text{CF}_4$ .

11. A method of etching a polysilicon layer on a substrate and simultaneously cleaning internal surfaces of a process chamber, the method comprising the steps of:

- (a) placing the substrate in the process chamber; and
- (b) exposing the substrate and the internal surfaces of the process chamber to an energized process gas comprising a bromine-containing gas including one or more of  $\text{HBr}$ ,  $\text{Br}_2$ , and  $\text{CH}_3\text{Br}$ ; a chlorine-containing gas including one or more of  $\text{Cl}_2$  and  $\text{HCl}$ ; an inorganic fluorinated gas including one or more of  $\text{NF}_3$ ,  $\text{CF}_4$ , and  $\text{SF}_6$ ; and an oxygen gas including one or more of  $\text{O}_2$  and  $\text{He-O}_2$ .

12. A method according to claim 11 wherein the volumetric flow ratio of the bromine-containing gas, chlorine-containing gas, inorganic fluorinated gas, and oxygen gas is selected so that the energized process gas etches regions

WO 00/04213

37

PCT/US99/14922

having different concentrations of dopant in the polysilicon layer at substantially the same etching rate.

13. A method according to claim 11 wherein the volumetric flow ratio of the bromine-containing gas, chlorine-containing gas, inorganic fluorinated gas, and oxygen gas is selected so that the energized process gas cleans off etch residue deposits formed on internal surfaces of the process chamber during etching of the polysilicon layer.

14. A method according to claim 13 wherein the volumetric flow ratio of the combined volumetric flow rates of the bromine-containing gas, chlorine-containing gas, and oxygen gas, to the volumetric flow rate of the inorganic fluorinated gas is from about 4:1 to about 20:1.

15. A method according to claim 11 wherein the volumetric flow ratio of the oxygen-containing gas and inorganic fluorinated gas is selected so that the energized process gas cleans off substantially all etch residue deposits formed on internal surfaces of the process chamber, and high selectivity of polysilicon to silicon dioxide.

16. A method according to claim 15 wherein the volumetric flow ratio of the volumetric flow rate of the oxygen gas, to the volumetric flow rate of the inorganic fluorinated gas is from about 1:1 to about 1:10.

17. A method according to claim 11 wherein the energized process gas consists essentially of HBr, Cl<sub>2</sub>, He-O<sub>2</sub>, and CF<sub>4</sub>.

18. A method of etching a polysilicon layer on a substrate in a process chamber, while simultaneously cleaning internal surfaces of the process chamber, the method comprising the steps of:

WO 00/04213

38

PCT/US99/14922

(a) placing the substrate in the process chamber, the substrate comprising a polysilicon layer having a first region with a first dopant concentration and a second region with a second dopant concentration; and

(b) exposing the polysilicon layer on the substrate and the internal surfaces of the process chamber to an energized process gas comprising a bromine-containing gas selected from the group consisting of HBr, Br<sub>2</sub>, and CH<sub>3</sub>Br; a chlorine-containing gas selected from the group consisting of Cl<sub>2</sub> and HCl; an inorganic fluorinated gas selected from the group consisting of NF<sub>3</sub>, CF<sub>4</sub>, and SF<sub>6</sub>; and an oxygen gas selected from the group consisting of O<sub>2</sub> and He-O<sub>2</sub>, wherein the volumetric flow ratio of the combined volumetric flow rates of the bromine-containing gas, chlorine-containing gas, and oxygen gas, to the volumetric flow rate of the inorganic fluorinated gas, is selected to etch the first and second regions at etching rates that differ by less than about 10%.

19. A method according to claim 18 wherein the volumetric flow ratio of the bromine-containing gas, chlorine-containing gas, inorganic fluorinated gas, and oxygen gas is selected so that the energized process gas cleans off the etch residue deposits formed on internal surfaces of the process chamber during etching of the polysilicon layer.

20. A method according to claim 18 wherein the energized process gas consists essentially of HBr, Cl<sub>2</sub>, He-O<sub>2</sub>, and CF<sub>4</sub>.

21. A method of etching a silicon-containing layer on a substrate in a process chamber, while simultaneously cleaning internal surfaces of the process chamber, the method comprising the steps of:

- (a) placing the substrate having the silicon-containing layer in the process chamber;
- (b) in a first etching stage, providing in the process chamber an energized first process gas comprising etching gas for etching the



WO 00/04213

39

PCT/US99/14922

silicon-containing layer on the substrate, and cleaning gas for cleaning deposits formed on the internal surfaces of the process chamber during etching of the silicon-containing layer;

(c) in a pump-out stage, stopping the flow of the first process gas and exhausting the energized first process gas from the process chamber; and

(d) in a second etching stage, providing in the process chamber an energized second process gas comprising etching gas for etching the silicon-containing layer on the substrate, the energized second process gas being substantially absent the cleaning gas.

22. A method according to claim 21 wherein the cleaning gas comprises an inorganic fluorinated gas selected from the group consisting of  $\text{NF}_3$ ,  $\text{CF}_4$ , or  $\text{SF}_6$ .

23. A method according to claim 21 wherein the etching gas comprises a bromine-containing gas selected from the group consisting of  $\text{HBr}$ ,  $\text{Br}_2$ , and  $\text{CH}_3\text{Br}$ , a chlorine-containing gas selected from the group consisting of  $\text{Cl}_2$  and  $\text{HCl}$ ; and an oxygen gas selected from the group consisting of  $\text{O}_2$  and  $\text{He-O}_2$ .

24. A method according to claim 21 wherein the pump-out stage comprises exhausting the energized first process gas from the process chamber until the process chamber is at a pressure of less than about 0.5 mTorr.

25. A method according to claim 21 wherein the pump-out stage comprises exhausting the energized first process gas from the process chamber for from about 5 to about 15 seconds.

WO 00/04213

PCT/US99/14922

1/5

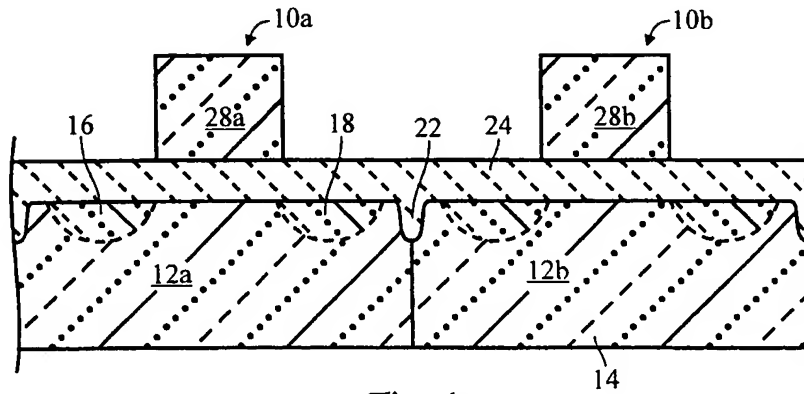


Fig. 1a

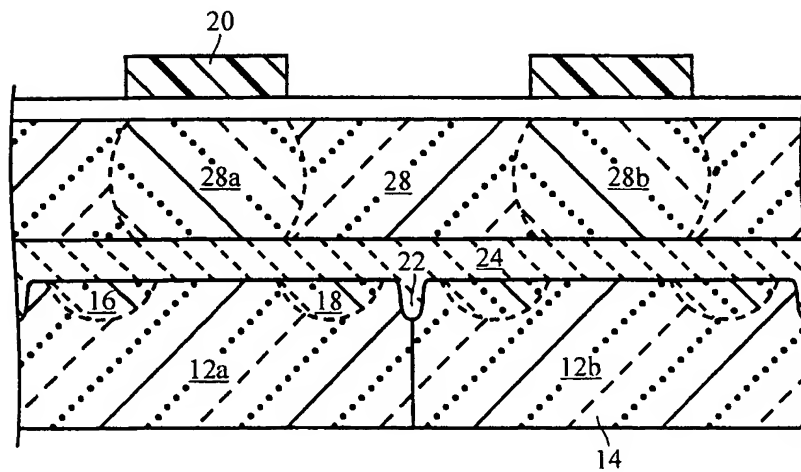
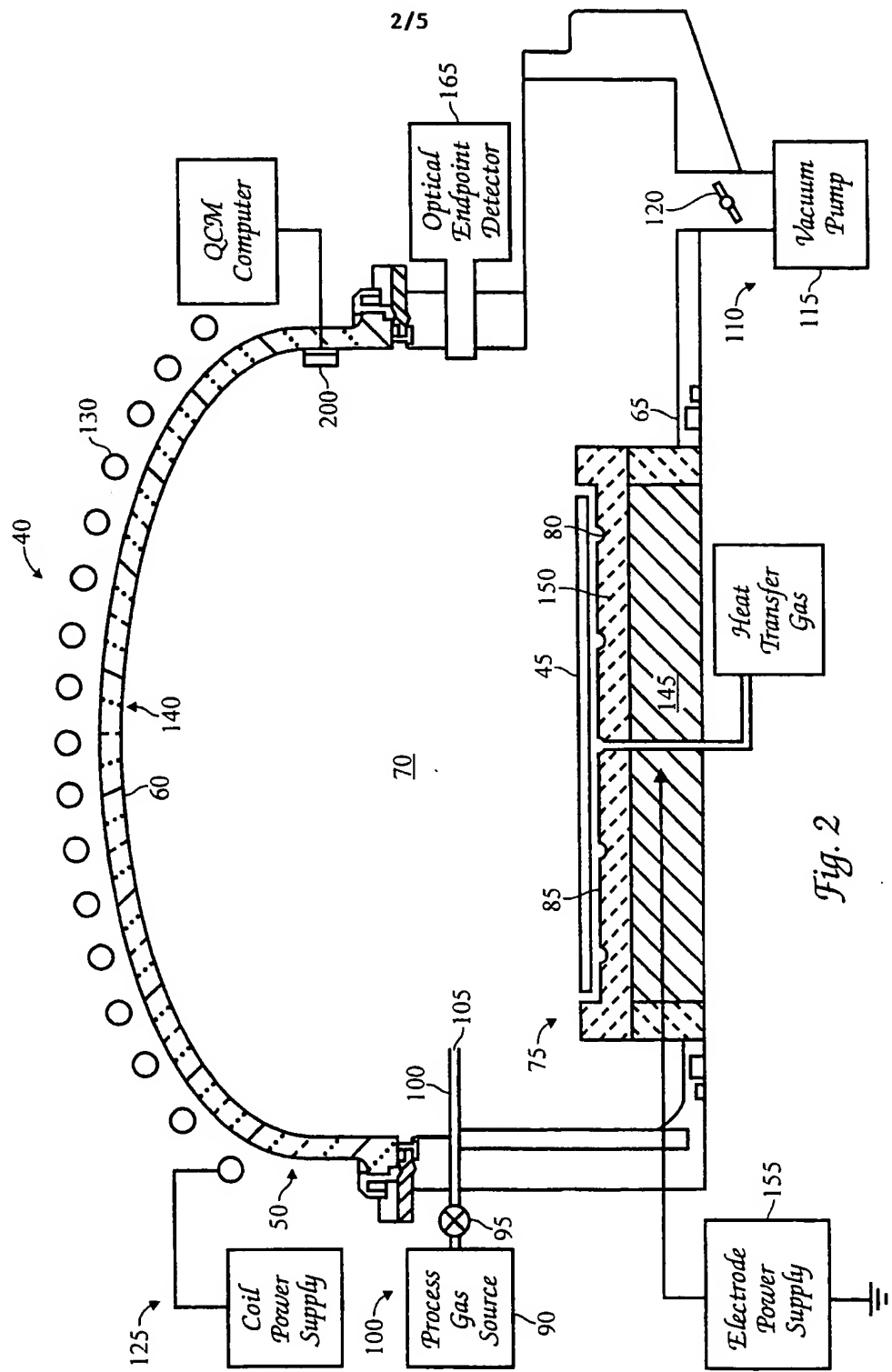


Fig. 1b



WO 00/04213

PCT/US99/14922

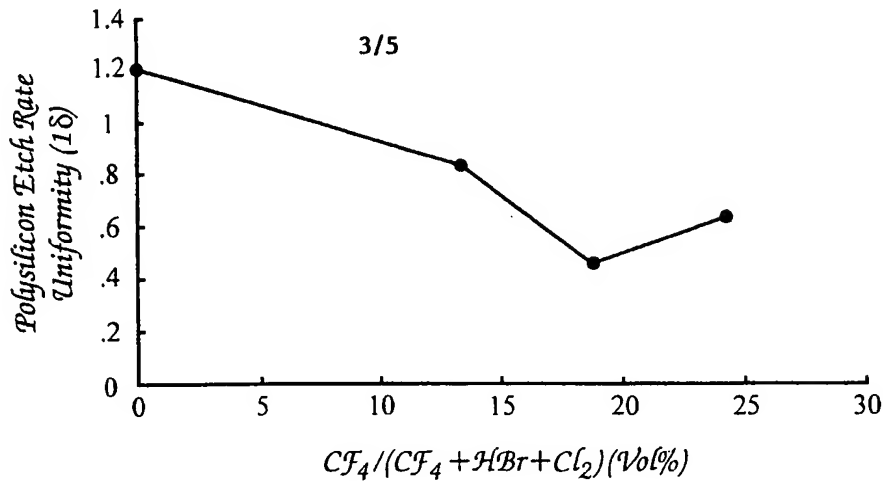


Fig. 3

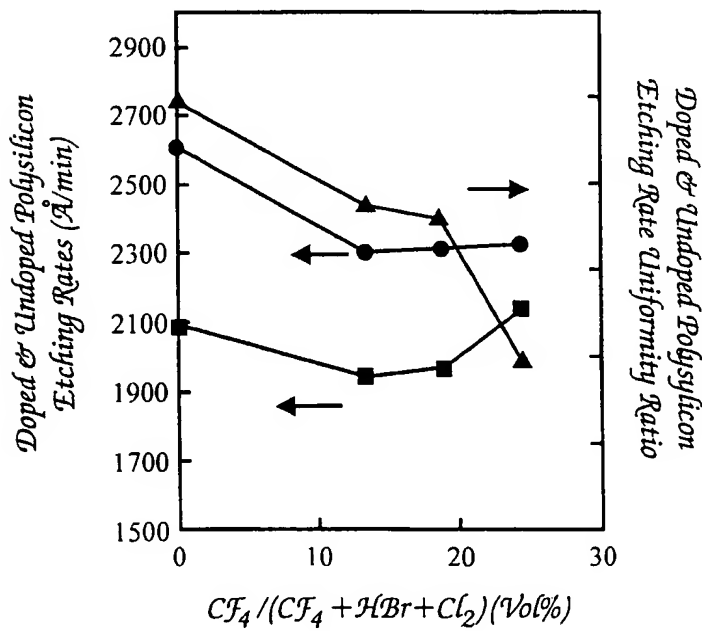


Fig. 4

WO 00/04213

PCT/US99/14922

4/5

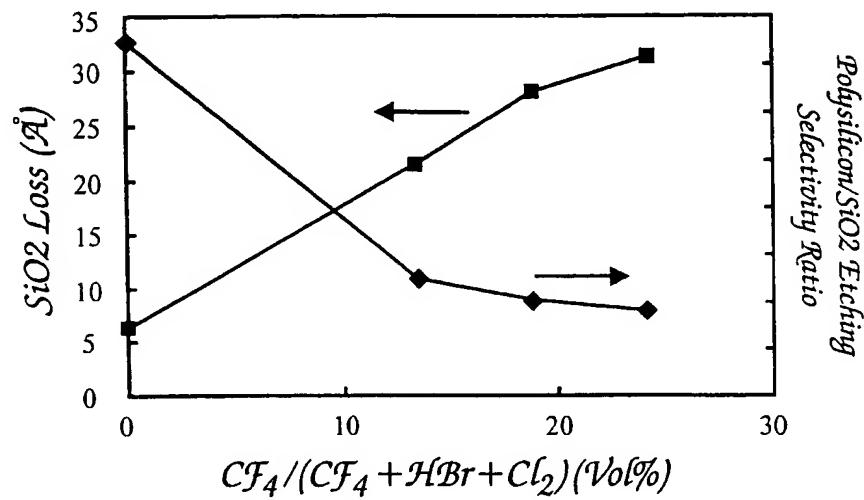


Fig. 5

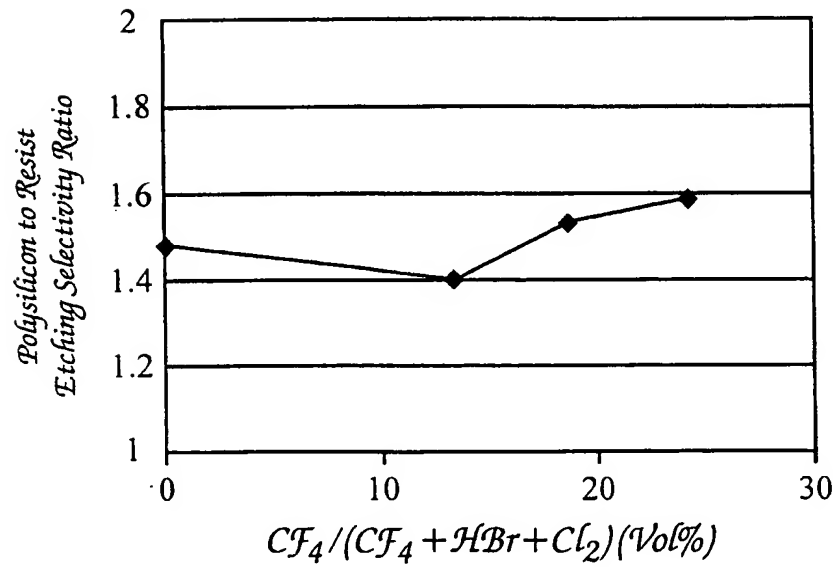


Fig. 6

WO 00/04213

PCT/US99/14922

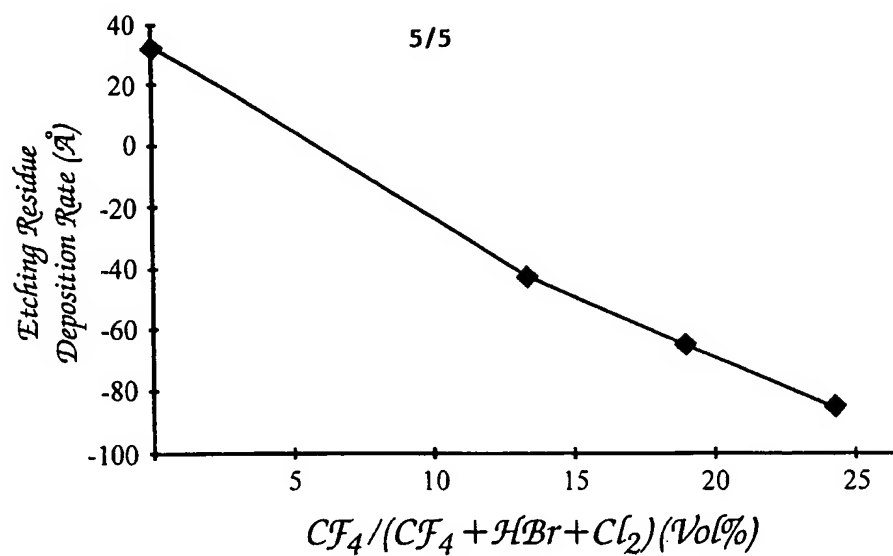


Fig. 7

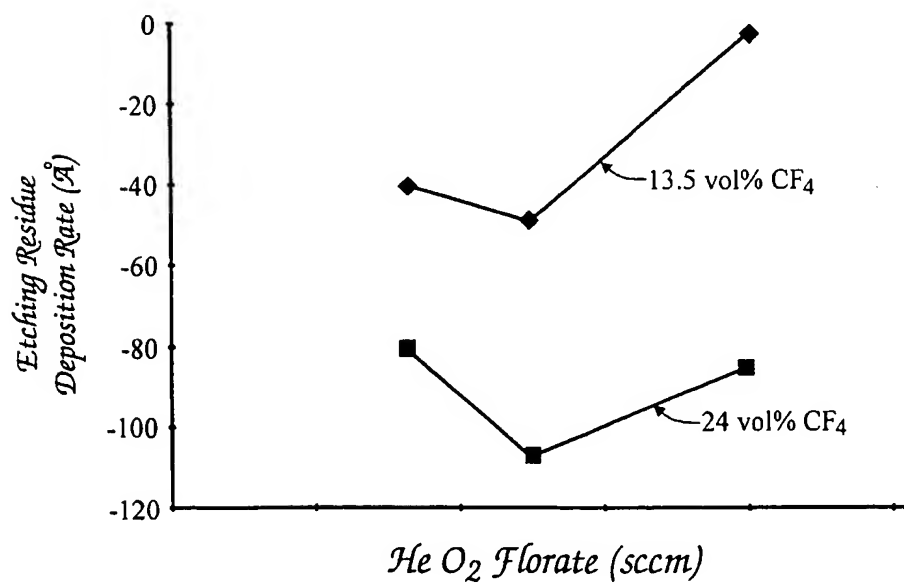


Fig. 8

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 99/14922

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 7 C30B33/12 H01L21/3065

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01L C30B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 272 143 A (APPLIED MATERIALS INC) 22 June 1988 (1988-06-22) page 4, line 13 -page 5, line 12 page 10, line 50 - line 55 page 12, line 1 -page 13, line 30	1,3-9, 11,13-16
X A	EP 0 314 990 A (MOTOROLA INC) 10 May 1989 (1989-05-10)  column 3, line 47 -column 5, line 24	1,5-8 4,9
X	US 5 767 021 A (IMAI SHINICHI ET AL) 16 June 1998 (1998-06-16) column 18, line 9 - line 63 column 23, line 9 -column 24, line 58; figure 17	1,3,8
	— -/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

18 October 1999

Date of mailing of the international search report

28.10.99

Name and mailing address of the ISA

European Patent Office, P.B. 6818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3018

Authorized officer

Köpf, C

## INTERNATIONAL SEARCH REPORT

Intern. Appl. No.  
PCT/US 99/14922

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 378 311 A (NAGAYAMA TETSUJI ET AL) 3 January 1995 (1995-01-03)	21,22, 24,25 23
A	column 3, line 67 -column 4, line 32; example 5	
A	EP 0 746 015 A (IBM CORP) 4 December 1996 (1996-12-04) column 2, line 6 -column 5, line 54	1,2,5,6, 8,18
A	US 5 318 668 A (TAMAKI TOKUHIKO ET AL) 7 June 1994 (1994-06-07) column 2, line 8 -column 5, line 48	21-23



International Application No. PCT/US 99/14922

**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

## Continuation of Box I.2

Present claims 21-25 relate to a large number of possible compounds ("a silicon-containing layer") to be etched by an unspecified etching gas and/or cleaning gas. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a limited number of the compounds claimed. In the present case, the claims so lack support, that a meaningful search over the whole of the claimed scope is impossible.

Consequently, the search has been carried out for those compounds which appear to be supported and disclosed, namely the etching of silicon-containing layers comprising doped or undoped silicon films, which can be crystalline (mono-/polycrystalline) or amorphous, metal silicides or combinations thereof commonly known as polycides, and silicon oxides, nitrides or oxynitrides. .

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 99/14922**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/14922

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0272143 A	22-06-1988	AT 177877 T	15-04-1999
		DE 3752259 D	22-04-1999
		DE 3752259 T	14-10-1999
		EP 0565212 A	13-10-1993
		JP 2071062 C	10-07-1996
		JP 7093291 B	09-10-1995
		JP 63278339 A	16-11-1988
		US 5874362 A	23-02-1999
EP 0314990 A	10-05-1989	US 4799991 A	24-01-1989
		DE 3889849 D	07-07-1994
		DE 3889849 T	05-01-1995
		JP 1230237 A	13-09-1989
		JP 2655336 B	17-09-1997
		KR 9711134 B	07-07-1997
US 5767021 A	16-06-1998	JP 8017740 A	19-01-1996
		US 5716494 A	10-02-1998
		JP 6077177 A	18-03-1994
		KR 126249 B	26-12-1998
US 5378311 A	03-01-1995	JP 6177091 A	24-06-1994
EP 0746015 A	04-12-1996	US 5665203 A	09-09-1997
		JP 8306672 A	22-11-1996
US 5318668 A	07-06-1994	JP 2677936 B	17-11-1997
		JP 5198538 A	06-08-1993